RI 8472

Bureau of Mines Report of Investigations/1980

Electrolytic Reduction of Chromium(VI) and Copper Using Coke Electrodes

By H. O. McDonald, D. M. Soboroff, and A. A. Cochran

UNITED STATES DEPARTMENT OF THE INTERIOR

I 28.23:

Report of Investigations 8472

Electrolytic Reduction of Chromium(VI) and Copper Using Coke Electrodes

By H. O. McDonald, D. M. Soboroff, and A. A. Cochran

UNITED STATES DEPARTMENT OF THE INTERIOR
Cecil D. Andrus, Secretary

BUREAU OF MINES
Lindsay D. Norman, Director

best copy available

This publication has been cataloged as follows:

McDonald, Hector O

Electrolytic reduction of chromium(VI) and copper using coke electrodes.

(Report of investigations • U.S. Bureau of Mines ; 8472)
Bibliography: p. 7.
Supt. of Docs. no.: I 28.23:8472.

1. Copper–Electrometallurgy. 2. Chromium–Electrometallurgy. 3. Reduction, Electrolytic. 4. Electrodes, Carbon. 5. Metals–Finishing–Waste disposal. I. Soboroff, David M., joint author. II. Cochran, Andrew A., joint author. III, Title. IV. Series: United States. Bureau of Mines. Report of investigations ; 8472.

TN23.U43 [TN780] 622s [669'.734] 80-607106

CONTENTS

	Page
Abstract	1
Introduction	1
Experimental procedures	3
Spent etchants	3
Coke-electrode cells	3
Results and discussion	6
Summary	7
References	8

ILLUSTRATIONS

1.	Small coke-electrode cell	4
2.	Schematic illustration of large coke-electrode cell	5
3.	Reduction of Cr^{6+} and copper electrowinning with fixed-bed coke electrodes	6

TABLES

1.	Composition of spent etchants	3
2.	Batch tests in small cell	6
3.	Batch tests in large cell	6
4.	Continuous test in large cell	7

ELECTROLYTIC REDUCTION OF CHROMIUM(VI) AND COPPER USING COKE ELECTRODES

by

H. O. McDonald,[1] D. M. Soboroff,[2] and A. A. Cochran[3]

ABSTRACT

Solutions containing Cr^{6+} and sulfuric acid are used in a number of surface-finishing operations. Substantial quantities of chromium and copper are lost and pollution problems are created when the spent solutions are discarded. To minimize the undesirable environmental effects while improving secondary resource recovery technology, the Bureau of Mines is conducting research to detoxify and recover metals from these solutions. Spent etchants are treated to remove copper and reduce Cr^{6+} to Cr^{3+} in an electrolytic cell. The anodes and cathodes are granulated coke. The spent solution is continuously pumped through the electrodes. Hexavalent chromium is reduced to trivalent chromium, and copper is recovered at the cathode. Reoxidation of Cr^{3+} at the anode was not observed. The removal and recovery of copper and reduction of Cr^{6+} lessen chemical demand and increase efficiency in waste treatment operations associated with the use of these solutions.

INTRODUCTION

The mission of the U.S. Department of the Interior, Bureau of Mines, is to insure the continued viability of the domestic minerals and materials economy and the maintenance of an adequate minerals base so that the Nation's economic, social, strategic, and environmental needs can be better served. Part of the research done in support of that mission has as its goals effecting pollution abatement and secondary resource recovery. In accordance with these activities, the objective of this investigation was to reduce toxic Cr^{6+} in various waste processing liquors to less toxic Cr^{3+} while simultaneously removing copper. In addition to recovering a valuable copper product,

[1]Research chemist (part-time), Rolla Research Center, Bureau of Mines, Rolla, Mo.; Associate Professor of Chemistry, University of Missouri-Rolla, Rolla, Mo.

[2]Research chemist, Rolla Research Center, Bureau of Mines, Rolla, Mo. (now with the Office of Water Research and Technology, U.S. Department of the Interior, Washington, D.C.).

[3]Supervisory research chemist, Rolla Research Center, Bureau of Mines, Rolla, Mo.

removal of copper and reduction of Cr^{6+} in these liquors will substantially decrease the chemical demand and increase efficiency in waste treatment operations associated with metallurgical processing.

Solutions containing Cr^{6+} (as chromic acid or sodium dichromate) and sulfuric acid are used in brass finishing, printed-circuit-board etching, preparation of plastics for plating, anodizing, and various other surface treatments. As the solutions are used, Cr^{6+} is reduced to Cr^{3+}, the dissolved-solids content increases, and the acid concentration is reduced. The action of this etchant on a copper substrate can be represented by the following equation:

$$Cr_2O_7^{2-} + 3\ Cu + 14\ H^+ \rightarrow 2\ Cr^{3+} + 3\ Cu^{2+} + 7\ H_2O.$$

The solutions are discarded when the reaction rate is below what is required for a given operation. At this point, a spent printed-circuit-board etchant, for example, would contain considerable amounts of Cu^{2+}, Cr^{3+}, and Cr^{6+}. A spent brass etchant would contain zinc in addition to these components. Technology for ultimate disposal of these wastes usually involves the reduction of the remaining Cr^{6+} to Cr^{3+}, followed by base addition to precipitate chromium and other metallic hydroxides. The resulting sludges are then used for landfill.

The disposal of these wastes in this manner is cause for environmental concern, and it wastes valuable resources. Current Environmental Protection Agency (EPA) regulations prohibit sewering of waste water containing more than 0.25 ppm Cr^{6+} and 4.6 ppm Cu^{2+} by plants discharging more than 38,000 l/day (10)[4]. Although the value of the copper recovered from these wastes is not particularly great at current prices, its recovery would save costs associated with its disposal. Landfill areas suitable for metal hydroxide sludges are becoming scarce, and collection, treatment, and disposal by waste contractors are expensive (7). Further, removal of copper from these wastes would make them more amenable to recovery and recycling.

Cochran and George (5) have shown that copper can be electrowon from spent brass etchant after all the chromium has been reduced. Several researchers successfully electrowon copper from dilute solutions using either porous electrodes or electrodes composed of small discrete particles. Bennion and Newman (3) used porous carbon anodes and cathodes to reduce the copper content of solution from 667 ppm to less than 1 ppm. Chu, Fleischmann, and Hills (4) and Paulin, Hutin, and Coeuret (8) reported similar results. Kennecott Copper Corp. (2) has operated a 100-lb/day prototype unit for recovering copper from dilute leach solutions. The unit uses thin particulate coke cathodes.

Copper has also been electrowon from dilute solutions using fluid-bed cathodes composed of either copper spheres (6) or chopped copper wire (9). Resource Control, Inc. (1), has designed a system to treat rinse water contaminated with electroplating wastes. The system uses a bed of "semiconductive carbonaceous material" between a standard anode and cathode.

---

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The system described in this report uses an electrolytic cell having coke anodes and cathodes. Spent brass and printed-circuit-board etchants are fed into the cell where Cr^{6+} is reduced to Cr^{3+} and copper is electrowon. This process differs from the prior art in that Cr^{6+} is reduced, and copper is electrowon from concentrated wastes in a single step using granulated coke electrodes. Granulated coke electrodes are inexpensive, inert, and readily available. The coke electrode, with the reduced copper metal, can be sold for its secondary copper value or furnaced directly to produce a copper ingot.

EXPERIMENTAL PROCEDURES

Spent Etchants

The compositions of the spent etchants used are given in table 1. Solution A is a spent printed-circuit-board etchant. Solution B is a spent brass etchant. Originally, both etchants were prepared from sodium dichromate and sulfuric acid. The compositions of etchants A and B are typical of solutions, in the application indicated, when they are ready to be discarded. The pH of these solutions ranges from 1.1 to 1.3. The compositions given are not to be regarded as representative of the exact point at which the solutions are discarded. The indicator of when the solutions are spent is often visual examination of the bath or product and not a chemical analysis.

TABLE 1. - Composition of spent etchants

Solution	Composition, g/l						Other elements present as spectrographic trace
	Cr^{3+}	Cr^{6+}	Cu	Zn	Na	$(SO_4)^{2-}$	
A.....	17	36	30	Trace	22	220	Ca, Mg, Sn.
B.....	31	5.3	45	19	15	290	Ca, Co, Fe, Mg, Mn, Ni, Pb, Si, Sn.

Coke-Electrode Cells

Small Coke-Electrode Cell

In the initial experiments, a small semicylindrical electrolytic cell containing one anode and one cathode was used (fig. 1). The cell was fabricated from Plexiglas[5] and contained five compartments separated by four polypropylene screens that contained the petroleum coke (minus 8- plus 16-mesh). It is conceptually similar to the large coke-electrode cell described later except that it contains only one pair of electrodes. A strip of lead was used as the anode current carrier. Electrical connection to the cathode was made using either nickel or copper strip. In some experiments, the coke was contained in a stainless steel basket that was then placed between a set of polypropylene screen dividers. The stainless steel basket served as the current carrier. This arrangement reduced corrosion of the current carriers at the electrolyte-air interface. The method of electrical connection did not affect the cathode efficiency.

[5]Reference to specific equipment (or trade names or manufacturers) does not imply endorsement by the Bureau of Mines.

FIGURE 1. - Small coke-electrode cell.

The current density was 2.15 amp/dm^2. (The area was calculated as if the electrodes were solid. Only the electrode area directly opposite another electrode was counted.) The actual current in the small cell was 2.7 amp at 2.7 to 2.5 volts. The current was kept constant throughout the operation of the cell. The voltage remained fairly constant throughout the trials.

The cell held 650 ml of solution. An additional 250 ml was kept in a separate container and circulated through the cell at a rate of 10 ml/min using a peristaltic pump.

Large Coke-Electrode Cell

This cell was constructed from a 30- by 30- by 30-cm polypropylene tank and held two anodes and two cathodes (fig. 2). Economical metallurgical coke (minus 8- plus 16-mesh) was held in four 30- by 30- by 1.9-cm holders fitted with polypropylene screen. Platinum strips embedded in the coke anodes served as current carriers; copper strips embedded in the cathodes served the same purpose. The electrode holders fitted snugly against the sides of the tank.

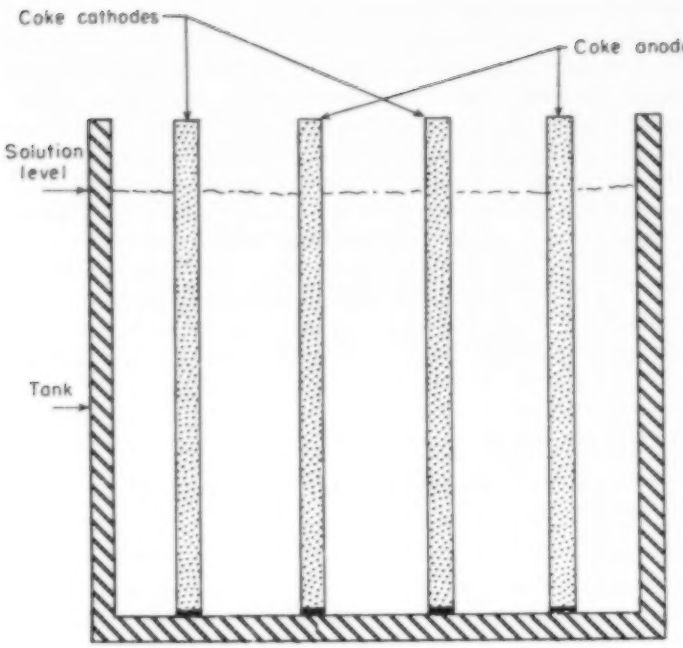

FIGURE 2. - Schematic illustration of large coke-electrode cell.

The current density in the large cell was 2.15 amp/dm^2. (This quantity was calculated in the same way as for the small cell.) The current was 42 amp at between ~6 and 4 volts. Voltage decreased as the operation proceeded. This cell is shown in figure 3.

The operating volume of the cell was 20 liters. A variable-flow positive-displacement pump was used for electrolyte circulation. When the large cell was operated in a continuous fashion, a peristaltic pump was used to feed spent etchant. The treated etchant was allowed to overflow the cell.

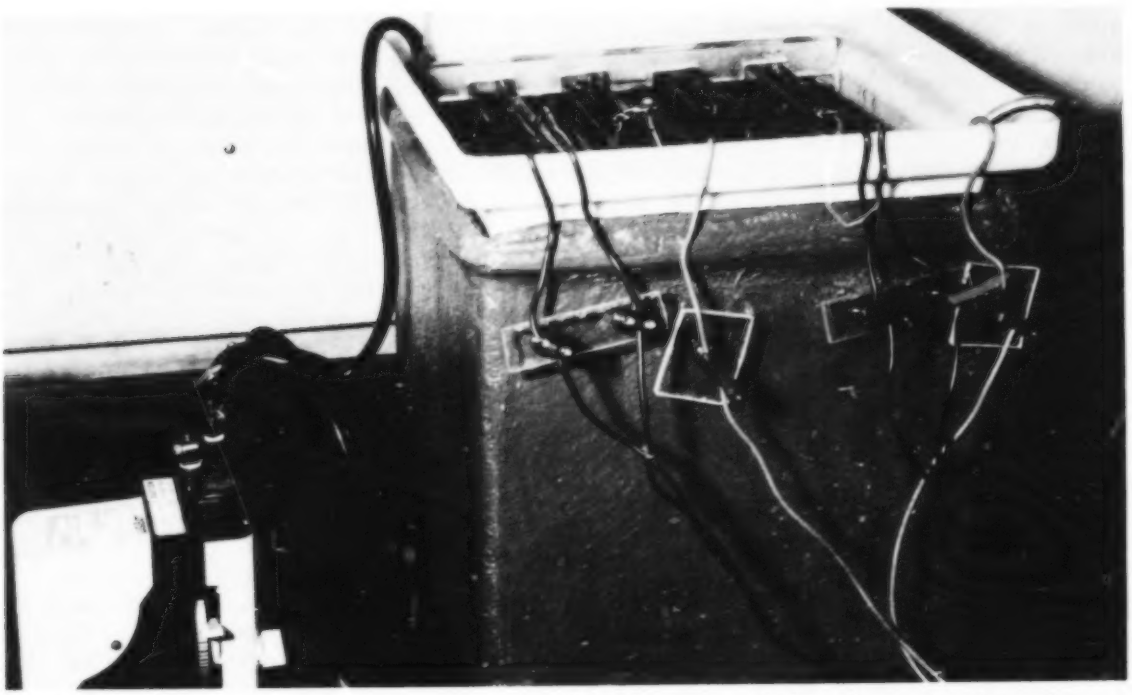

FIGURE 3. - Reduction of Cr^{6+} and copper electrowinning with fixed-bed coke electrodes.

RESULTS AND DISCUSSION

The reduction of Cr^{6+} to Cr^{3+} and copper electrowinning were achieved with both the spent printed-circuit-board etchant and the spent brass etchant. Significant pH changes were not observed during the electrolysis. Table 2 gives the results of batch treatment of the spent printed-circuit-board etchant in the small cell. Efficiencies were calculated on the basis of total equivalents of copper and Cr^{3+} produced. These data indicate that simultaneous Cr^{6+} reduction to Cr^{3+} and copper deposition occurred with fairly good efficiencies during the initial ~45 pct of the trial. There were two major problems with this cell: severe corrosion of the current carriers and short-circuiting. Anode and cathode surfaces were within 1.3 cm of each other. Growth of dendritic copper on the electrode surface usually short-circuited the cell after about 48 hours.

TABLE 2. - Batch tests in small cell

Trial	Composition, g/l			Time, hr	Current efficiency, pct
	Cr^{3+}	Cr^{6+}	Cu		
At start.....	17	36	30	0	NAp
1.....	42	11	14	22	80
1.....	46	7.5	4.4	46	48
2.....	41	12	15	19	87

NAp Not applicable.

The large cell was constructed to correct these problems. Electrode spacing was 4 cm (surface of the cathode to surface of the anode). Platinum strips embedded in the coke anodes and copper strips in the cathodes were used as current carriers, which solved the corrosion problem. Table 3 gives the results of batch tests in the large cell at various circulation rates. Initially, efficiencies appear to be better at the lower circulation rates; however, dendritic copper growth on the cathode is less severe at higher rates. In 48 hours, only 0.02 g/l Cu or less and no detectable amount of Cr^{6+} remained in the treated etchant in all of the tests. Variance in the amount of Cr^{3+} and zinc in the solution is the result of volume changes during the electrolysis. (Water was added periodically to make up evaporation losses.) No short-circuiting problems were encountered during the batch tests.

TABLE 3. - Batch tests in large cell

Trial	Composition, g/l				Circulation rate, ml/min	Time, hr	Current efficiency, pct
	Cr^{3+}	Cr^{6+}	Cu	Zn			
At start.....	31	5.3	45	19	NAp	0	NAp
1.....	40	ND	1.6	20	6.7	24	89
	38	ND	.01	19	6.7	48	46
2.....	37	.17	2.4	22	30	24	86
	37	ND	.02	21	30	48	45
3.....	37	.31	12	20	80	25	66
	40	ND	.02	21	80	48	45

NAp Not applicable.
ND Not detected.

The results of continuous operation of the large cell are presented in table 4. Twenty liters of spent brass etchant was placed into the cell and electrolyzed for 24 hours. Spent etchant was then fed into the cell at 14 ml/min, and treated etchant was removed through an overflow tube located near the top of the cell. Etchant in the cell was agitated by circulating the solution with a positive-displacement pump at 100 ml/min. The circulation was from anode to cathode.

TABLE 4. - Continuous test in large cell

Time, hr	Voltage	Composition, g/l			
		Cr^{3+}	Cr^{6+}	Cu	Zn
0.....	5.9	31	6	45	19
24.....	4.8	39	.53	15	22
48.....	4.4	38	1.2	9.5	21
72.....	4.3	38	.85	5.5	21
96.....	3.9	40	.71	4.2	21

The higher circulation rate was chosen to minimize dendritic copper formation and subsequent short-circuiting. No problems with short-circuiting were encountered during the trial, but an examination of the cathodes after the run showed a substantial buildup of copper metal on the polypropylene screens. This copper buildup resulted in an increase in efficiency because the electrode was rendered more conductive.

Overall, 81 pct of the copper was removed and 86 pct of the Cr^{6+} was reduced to Cr^{3+} at a current efficiency of 52 pct in the continuous run. The power requirement of copper electrowinning is about 6.6 kwhr/kg (3 kwhr/lb) for the spent brass etchant. This is essentially the same power requirement as Kennecott's process for winning copper from dilute leach solutions (2).

It appeared that no Cr^{3+} was oxidized at the coke anode. Small anode weight losses were observed.

SUMMARY

The reduction of Cr^{6+} while simultaneously removing copper from spent brass and printed-circuit-board etchants has been demonstrated. Using an electrolytic cell fitted with coke anodes and cathodes, 81 pct of the copper was removed from a spent brass etchant and 86 pct of the Cr^{6+} was reduced to Cr^{3+} in continuous operation. The technique described has potential for simplifying the disposal of these waste etchants as well as for recovering a valuable copper product, although EPA limits for Cr^{6+} and Cu have not been achieved in this study.

REFERENCES

1. American Machinist. Electrochemical Unit Treats Plating Wastes. V. 114, No. 3, Feb. 23, 1970, pp. 94-95.

2. Ammann, P. R., G. M. Cook, C. Portal, and W. E. Sonstelie. Direct Electrowinning Copper From Dilute Leach Solutions. Ch. in Extractive Metallurgy of Copper, ed. by J. C. Yannopoulos and J. C. Agarwal. Port City Press, Baltimore, Md., v. 2, 1976, pp. 995-1008.

3. Bennion, D. N., and J. Newman. Electrochemical Removal of Copper From Very Dilute Solutions. J. Appl. Electrochem., v. 2, No. 2, 1972, pp. 113-122.

4. Chu, A. K. P., M. Fleischmann, and G. J. Hills. Packed Bed Electrodes. I. The Electrochemical Extraction of Copper Ions From Dilute Aqueous Solutions. J. Appl. Electrochem., v. 4, No. 4, 1974, pp. 323-330.

5. Cochran, A. A., and L. C. George. Recovery of Metals From a Variety of Industrial Wastes. Res. Recovery and Conserv., v. 2, No. 1, 1976, pp. 57-65.

6. Fleischmann, M., J. W. Oldfield, and L. Tennakoon. Fluidized Bed Electrodes. IV. Electrodeposition of Copper in a Fluidized Bed of Copper-Coated Spheres. J. Appl. Electrochem., v. 1, No. 2, 1971, pp. 103-112.

7. Hallowell, J. B., L. E. Vaaler, J. H. Gurklis, and C. H. Layer. Assessment of Industrial Hazardous Waste Practices--Electroplating and Metal Finishing Industries--Job Shops. Battelle's Columbus Laboratories (Columbus, Ohio), EPA Rep. September 1976, p. 128; available from the National Technical Information Service, Springfield, Va. PB 264 349.

8. Paulin, M., D. Hutin, and F. Coeuret. Theoretical and Experimental Study of Flow-Through Porous Electrodes. J. Electrochem. Soc., v. 124, No. 2, 1977, pp. 180-188.

9. Simpson, C. F. Purity of Copper Produced by Fluid Bed Electrolysis of a Heap-Leach Solution. J. Metals, v. 30, July 1977, pp. 6-10.

10. U.S. Code of Federal Regulations. Title 40--Proposed Pretreatment Standards for Existing Sources; Chapter I--Environmental Protection Agency; Subchapter N--Effluent Guidelines and Standards; Part 413--Electroplating Point Source Category. Federal Register, v. 43, No. 31, Feb. 14, 1978, pp. 6560-6573.

☆U.S. GOVERNMENT PRINTING OFFICE: 1980-603-102/90

INT.-BU.OF MINES,PGH.,PA. 24810